

8<sup>th</sup> International Conference on Photonic Technologies LANE 2014

## Pattern Transfer of Sub-micrometre-scaled Structures into Solid Copper by Laser Embossing

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### Abstract

Laser embossing allows the micron and submicron patterning of metal substrates that is of great interest in a wide range of applications. This replication process enables low-cost patterning of metallic materials by non-thermal, high-speed forming which is driven by laser-induced shock waves. In this study the surface topography characteristics as well as the material structure at laser embossing of sub-micrometre gratings into solid copper is presented. The topography of the laser-embossed copper pattern is analysed with atomic force microscopy (AFM) in comparison to the master surface. The height of the embossed structures and the replicated pattern fidelity increases up to a laser fluence of  $F \sim 10 \text{ J/cm}^2$ . For higher laser fluences the height of the embossed structures saturates at 75% of the master pattern height and the shape is adequate to the master. Structural modifications in the copper mono crystals after the laser embossing process were investigated with transmission electron microscopy (TEM) and electron backscatter diffraction (EBSD). Almost no modifications were detected. The residual stress after laser embossing of 32 MPa ( $F = 30 \text{ J/cm}^2$ ) has only a limited influence on the surface pattern formation.

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Peer-review under responsibility of the Bayerisches Laserzentrum GmbH

**Keywords:** laser embossing; laser shock processing; forming; laser

### 1. Introduction

Structuring of surfaces with micron and submicron patterning is of great interest for a wide range of applications. A typical low-cost method to generate such structures is microembossing. However, microembossing is mostly applied for soft materials like polymers [1-3]. Microembossing of metals is limited to their formability due to the

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size effect [4-6], durability of the moulds [7] and processing speed. A microembossing method which overcomes these limitations is laser embossing. Laser embossing is based on laser-induced shockwaves for plastic microforming of work pieces. Laser embossing has great potential in the field of micro- to nanostructuring because of high precision, high repeatability, flexibility and high throughput which enables mass production.

Laser embossing is a laser shock processing (LSP) method that is characterized by a high strain rate with typical values of  $10^6$ - $10^8$  s<sup>-1</sup>. Up to now the focus of the characterization of the laser embossing process has been on thin metal foils in which structures with sizes in the micrometre range were embossed in the solid state [6, 8-13]. Only a few studies have been published in which laser embossing processes into solids were investigated [14-16]. A limited number of studies concentrated on laser embossing of submicron structures in metals. The precise embossing of submicron structures in metals is restricted because of the poor formability of these materials in the solid state. The precise formability of metals in the sub-micrometre range is limited mainly due to fluctuations in plasticity [17] and size strengthening effects [4-6]. G.J. Cheng has shown that laser embossing is able to overcome these problems by demonstration of nanoscale laser embossing into aluminium foils [17].

In the present study laser embossing of sub-micrometre structures in copper solids is investigated with two aims. First the formability of solid copper samples in the submicron range by laser embossing is systematically studied by embossing periodic 450 nm patterns in polycrystalline solid copper. Secondly, microstructure modifications of the copper due to the laser embossing process are analysed. For this investigation sub-micrometre structures were embossed in differently oriented copper monocrystals. The processed samples were analysed by transmission electron microscopy (TEM) in order to detect nucleation of defects, the generation of an amorphous surface layer, or other crystal structure modifications. To analyse the residual stress and possible crystal modifications in the monocrystalline copper, X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) analyses were performed. For the EBSD and XRD investigations unstructured flat masters were embossed into the monocrystalline copper to exclude geometrical effects which could interfere with the EBSD analyses.

## 2. Experimental Set-up

In this study the laser embossing of submicron patterns was performed into polycrystalline and monocrystalline copper samples with a size of 1 cm x 1 cm and a thickness of 500 µm. 8 µm thick nickel foils which were produced by electro plating were used as master forms. Nickel was selected as the material for the master form because the master form material has to be of a higher stiffness and strength than the workpiece. Hence with a master form made from nickel the workpiece material is currently restricted to ductile materials, e.g. copper, silver, lead and gold. The surface structure of these master foils is a 2D grating structure (period of 450 nm, height (peak-to-valley) of 110 nm) which is shown in Fig. 2. In addition an unstructured flat nickel foil was used as a master form, too. According to the inverse laser embossing approach [15, 16] the masters were placed on top of the copper samples. The mechanical energy for the embossing process is provided by the laser-induced shock waves. The shock waves were induced by the ablation of a polyimide (PI) foil which is placed on top of the nickel master foils. In Fig. 1 a sketch of the experimental arrangement is shown. The PI foil also protects the sample from the thermal impact of the laser pulses and from contamination of debris generated by the ablation process of the PI foil. Because of the low thermal conductivity of the PI foil, a remaining thickness of ~ 3 µm of the PI foil is sufficient to insulate the workpiece and the master used from the thermal impact of the laser pulses.

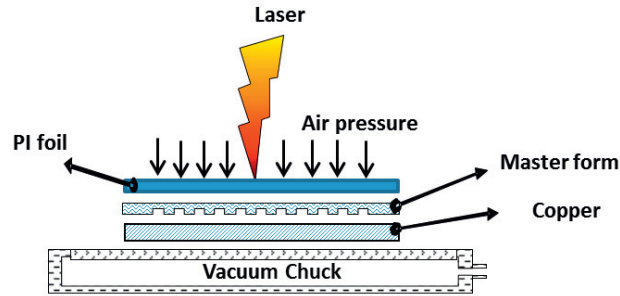


Fig. 1. Cross section of the experimental set-up of inverse laser embossing applied in this study.

The vacuum chuck ensures close contact between the PI foil/master/sample stack due to the surrounding air pressure (see Fig. 1). A KrF excimer laser with a pulse length of  $t_p = 25$  ns and a wavelength of  $\lambda = 248$  nm embedded in a laser workstation (Exitech, Ltd.) was used as the laser source. The shock wave pressure is primarily determined by the laser pulse intensity  $I$  which is used for the ablation of the PI foil. According to the model of C.R. Phipps [18] the pressure  $P$  can be estimated by the empiric trend:

$$P \propto b * I^{n+1} * \lambda^n * \tau^{\frac{n}{2}}$$

with wavelength  $\lambda$  of the laser radiation, laser pulse duration  $\tau$ ,  $b$  and  $n$  experimental coefficients.

After the laser embossing process the samples were analysed with atomic force microscopy AFM (Dimension FastScan AFM (Bruker), FastScan A cantilever, nominal tip radius  $< 5$  nm), electron backscatter diffraction (EBSD) (embedded 3D- Nanoanalyse-Cross-Beam-System-FIB Auriga 60) and transmission electron microscopy (TEM) (Titan3<sup>TM</sup> 60-300 S/TEM). In order to characterize the residual stress in the samples, X-ray diffraction (XRD) (Rigaku Ultima IV) was performed.

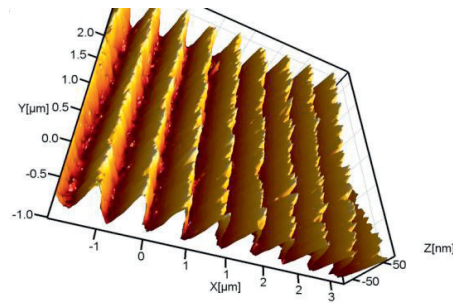


Fig. 2. 3D AFM-image of the surface structure of the Ni master form produced by electroplating.  
The height profile is shown in Fig. 3.

### 3. Results and Discussion

The structures of the masters were replicated by laser embossing into polycrystalline copper samples to investigate the formability of copper in the submicron range and to evaluate the precision and the pattern fidelity of the laser-embossed replica. The replicated structures were analysed by AFM. Profiles of the surface topography from the master (inverted) and from the replicated structures laser-embossed with different parameters are shown in Fig. 3 (left). The comparison of the shape and period of the replicated structures with the original structures of the master form shows good conformity for high laser fluences. However, the height of the replicated structures is less

than the height of the master structures even for the highest laser fluences used. The height of the replicated structures in dependence on the laser fluency used for the laser embossing process is shown in Fig. 3 (right). The height of the replicated structures increases with rising laser fluence and reaches the maximum height of  $\sim 70$  nm at a laser fluence of  $\sim 10$  J/cm<sup>2</sup>. A laser fluence of  $F = 10$  J/cm<sup>2</sup> corresponds according to (1) to a pressure of  $P \sim 0.23$  GPa. The usage of higher laser fluences does not result in higher replicated structures although the height of the master form structures with  $\sim 110$  nm is not reached. The reason for this was found in the elastoplastic properties of the metals. The elasticity of the nickel foil and the copper sample causes a spring back after laser embossing.

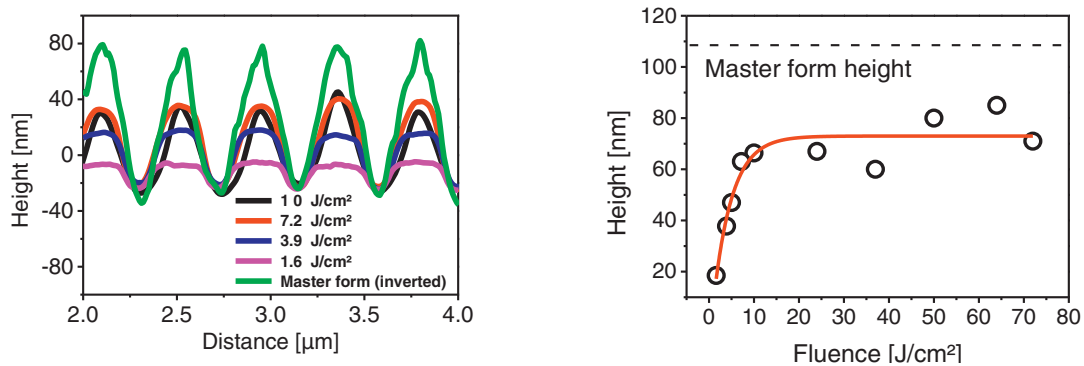


Fig. 3. (left) Height profile of the replicated structures, for comparison the inverted height profile of the master form is also shown in this image. The height profiles were measured by AFM; (right) Height of the replicated structure in the copper work piece in relation to the laser fluence. The red line is for visual effect.

To investigate possible microstructure modifications due to the laser embossing process, TEM analyses were performed. In Fig. 4 an exemplary TEM image of an embossed form master structure into a monocrystalline  $\langle 100 \rangle$  oriented copper sample is shown. The laser fluence used was  $F = 30$  J/cm<sup>2</sup>. A thin platinum film was deposited for protection of the sample's surface during the necessary sample preparation. As seen in the TEM image, no significant growth of the defect density or other modifications near the embossed structure could be found. A magnified section of the sample area that is marked with the circle in Fig. 4 (left) is shown in Fig. 4 (right). Also, in the magnified image, no indication for an increased defect density, sub grain formation, or surface amorphisation could be found.

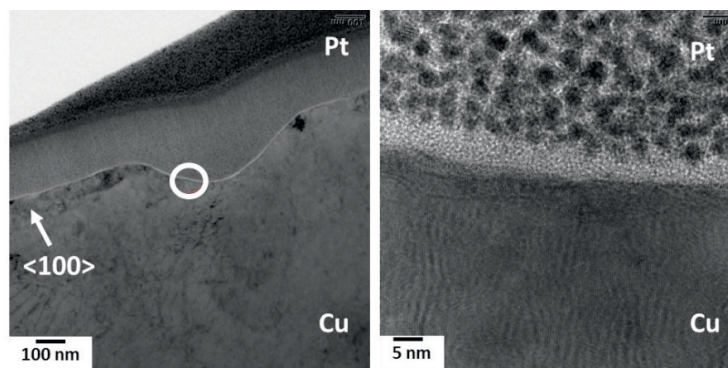


Fig. 4. TEM-image of a  $\langle 100 \rangle$  oriented copper mono crystal. In the copper mono crystal sub-micrometre structures were embossed. For protection the sample surface was covered with a thin platinum film. In the right figure a magnified image of the sample is shown that is marked in the left figure with a circle.

For the EBSD analyses the flat surface of an unstructured nickel foil was embossed into monocrystalline copper to avoid interference of the EBSD results by the inclined surface topography. In Fig. 5 an EBSD analysis before (left) and after (right) of the embossing process is shown. The black stripes in the EBSD image of the processed sample surface are caused by polishing defects and carbon contaminations (as seen in SEM – not provided) that are not related to the laser embossing process. By comparison, the EBSD images of the unprocessed and processed sample surface it can be seen that no new orientated grains in the monocrystalline copper are generated. Similarly, the distribution of the misorientation is not altered due to the embossing process as can be seen in the histogram in Fig. 5 (bottom).

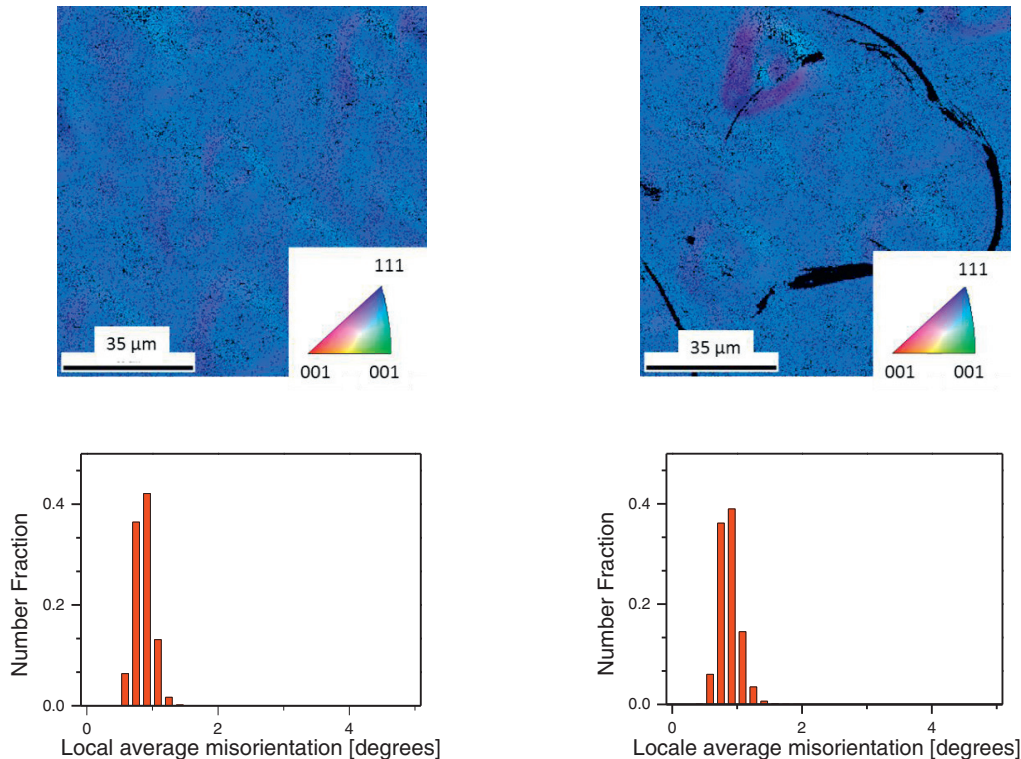


Fig. 5. (top) grain orientations <111> oriented copper mono crystal before (left) and after laser embossing (right). Figure 5 (bottom) misorientation before (left) and after (right) laser embossing.

The results of the EBSD evaluation are in agreement with the TEM analysis which also saw no significant alteration of the grain orientation nor could the generation of new grains be detected which was observed in other studies with higher laser shock pressure used [19, 20].

With the former results the mechanism of laser embossing in particular of submicron patterns into monocrystalline copper could not be explained completely. Therefore, X-ray diffraction (XRD) measurements were performed at laser-embossed samples.

A rough estimation of the residual stress in the monocrystalline copper sample can be done by XRD measurements. The XRD analyses were performed before and after the flat nickel foil master was embossed on to a <100> oriented monocrystalline copper sample. From the 2-theta scan the lattice constant  $l$  of the samples was calculated by Bragg's law:

$$2d\sin\theta = n\lambda$$

with  $\lambda$  wave length,  $n$  is diffraction order,  $\theta$  Bragg angle, and  $d$  lattice spacing. For a laser fluence of  $F = 30 \text{ J/cm}^2$  a lattice constant of  $1.80003 \text{ \AA}$  was calculated that is  $\sim 0.3\%$  less than the value which was measured for the unprocessed  $\langle 100 \rangle$  Cu sample. Supposing that the changing of the lattice constant is one-dimensional in the direction of the incident shock wave, the stress can be estimated by Hooke's law.

$$\sigma = E * \frac{l_0 - l_1}{l_0}$$

with  $l_0$ ,  $l_1$  lattice constant of the sample before and after loading with shock wave pressure and  $E$  Elastic modulus ( $E = 168 \text{ GPa}$ ) of the monocrystalline copper sample. The calculated residual stress in the sample due to laser embossing at a laser fluence of  $F = 30 \text{ J/cm}^2$  was  $\sigma \sim 32 \text{ MPa}$ . Assuming that the compression stress is homogeneously distributed in the direction of the incident shock wave the thickness reduction is  $\sim 95 \text{ nm}$  of the  $500 \text{ }\mu\text{m}$  thick monocrystalline copper sample according to Hooke's law. Although the calculated thickness reduction is in the same range as the height of the laser-embossed structures, the mechanism of surface structure formation by laser embossing can be assigned not only by material compression even when it is assumed that higher residual stresses occur in the laser-embossed submicron patterns. This is related to the fact that the pattern height referring to material compression is limited to a depth in the sample that features an almost constant stress. With this assumption the material compression can only contribute in part to the laser-embossed surface pattern height. Because the TEM and EBSD analysis data show almost no significant microstructure modifications (defects, misaligned crystals etc.) near the surface, the main laser-embossed pattern height is related to plastic deformation. This plastic deformation is induced by a plastic flow along the direction of the activated slip systems. Therefore, defects and other structural modifications can be accumulated in deeper material regions as shown in [19, 21, 22].

#### 4. Summary

It has been shown that precise submicron structures can be fabricated by laser embossing into copper samples. The shapes of the master form structures are precisely transferred into the copper surface at high laser fluences but the pattern height is significantly less than the master pattern's height. By increasing the laser fluence up to  $F \sim 10 \text{ J/cm}^2$  the height of the replicated structures increase and the shape is progressively approximating the master surface. At a particular laser fluence, the pattern height saturates and the shape does not change further. TEM and EBSD analysis of laser-embossed, monocrystalline copper samples show almost no significant modifications of the sample material microstructure near the surface so that laser embossing can be considered as a nearly damage-free structuring method for copper solids. The residual stress which is induced by the laser embossing process was estimated from XRD analyses to be in a range of  $\sim 30 \text{ MPa}$ . The pattern formation is mainly related to plastic deformation due to the material slip system but residual compressive stress in the patterned surface can also contribute to the pattern height.

#### Acknowledgements

The authors would like to thank Dr. M. Himmerlich for fruitful scientific discussions. The funding from the German Research Foundation (Deutsche Forschungsgemeinschaft – DFG) is highly acknowledged. The authors acknowledge the help of Ms Salamatina with the preparation of the manuscript.

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